

Safe Lithium-ion Battery Designs for Use, Transportation and Second Use



Judy Jeevarajan, Ph.D.
Underwriters Laboratories Inc.

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Introduction

- Lithium ion batteries are being used in ground, aviation, space, sea, etc. applications in various sizes
- Introduced in recent years into the utility/stationary energy storage industry
- Energy Storage Industry deployed 40.7 MW of capacity in Q2 2015 (9 times compared to Q2 2014)
 - Other cumulative installations totalled 5.6 MW
 - Total ~ 50 MW in 2015
 - Goal: Build or Purchase 1.3 GW of storage by 2020 in California
- Automotive batteries are being repurposed for utility/stationary storage applications
- With increasing energy density at the cell level and with the need for high voltage, high capacity, high power battery systems, questions arise on the safety of the battery systems
 - Has a detailed FMEA/FTA been created for the energy storage system?
 - Have all the system level hazards been addressed?
 - Has extensive testing been carried out at all levels to confirm that safety controls designed at each level work as expected – cell, module, battery, etc.
 - Does the safety change with other factors?
 - Size of battery?
 - Environments (temperature, pressure, dust, humidity, vibrations, etc.)?
 - Cycle and calendar life (including storage)?
 - Special transportation needs and safety during transportation?
 - Other unique requirements?



Growth in Size of Batteries used for Various Applications

Challenges:

- **Cell to Module to Battery Level Scale-Up**

Cell level controls do not necessarily translate to module or battery level controls

- **Testing in the Relevant Environment**

All safety controls need to be verified by testing at the appropriate level and in the relevant environment

Example: Hazards such as overcharge and external short have opposite outcomes in pressurized versus non-pressurized environments due to the difference in heat dissipation

Battery Manufacturing Process Challenges

- Tens of thousands to billions of cells manufactured for different types of applications from portable equipment to large ESS.
- Challenge is to **screen and match** every individual cell.
 - Typical COTS and some custom battery manufacturing process does not include cell screening and matching.
 - Cells are assembled into batteries in the ‘as received’ condition at lower SOC (typically 40%)
- Are assembled batteries **tested under relevant stringent** conditions before sent out into the field?
- Battery **certification tests** that are **comprehensive enough** with **stringent pass/fail criteria**
- Certification tests that verify the **operation of the safety controls** designed into the battery

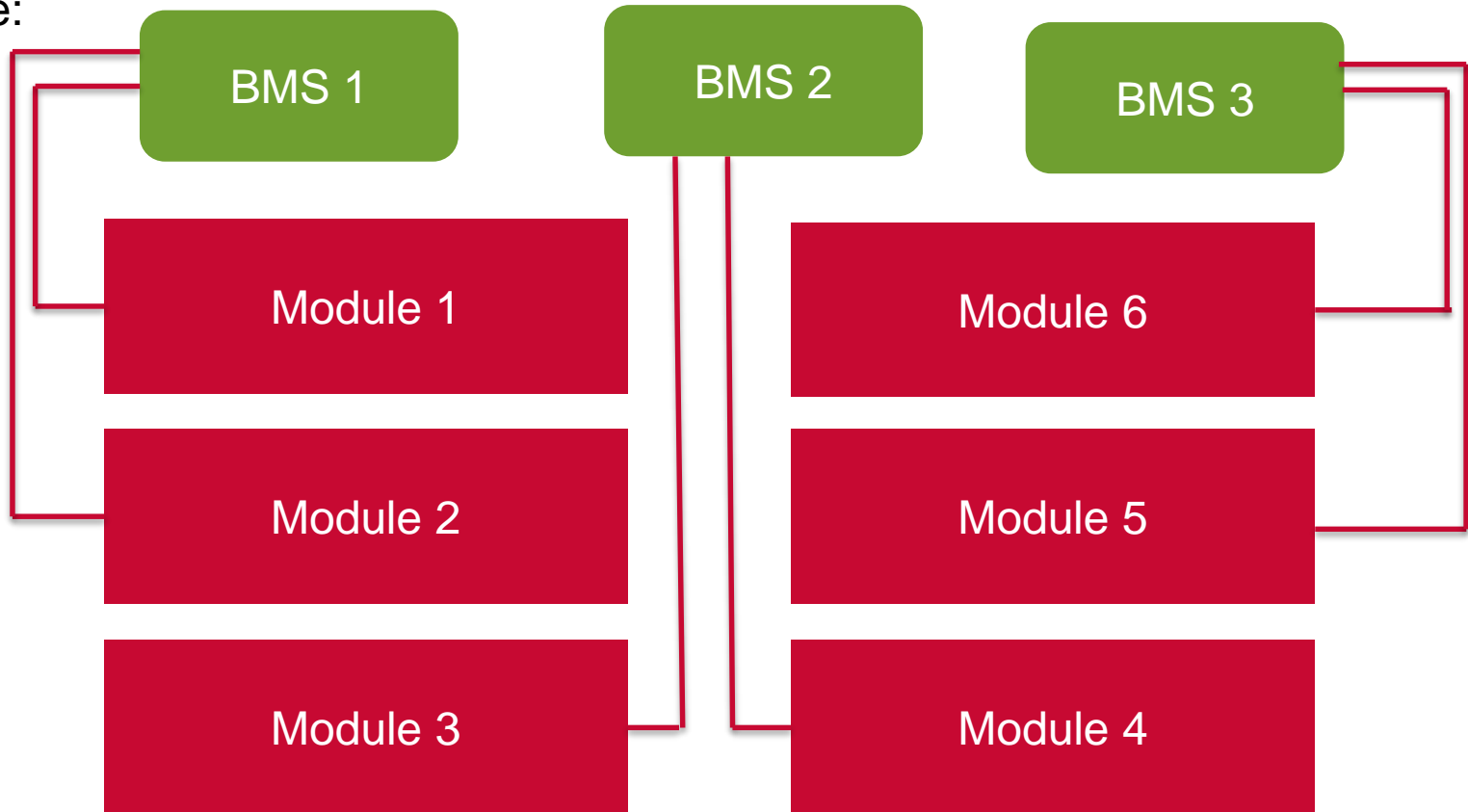
Challenges with Large Battery Designs

Thermal Gradient



Deviations: Voltage,
capacity, internal
resistance/impedance
Eventually safety is ?

Example:



Forced Air Cooling Inlets at one end of Battery

Other Challenges

High
Voltage
Safety

Complexity of sensing
systems / BMS

Quality of
Sensors,
electronics,
protective
devices,
software

Flammability
and
Offgassing

Fire
Extinguishing
methods

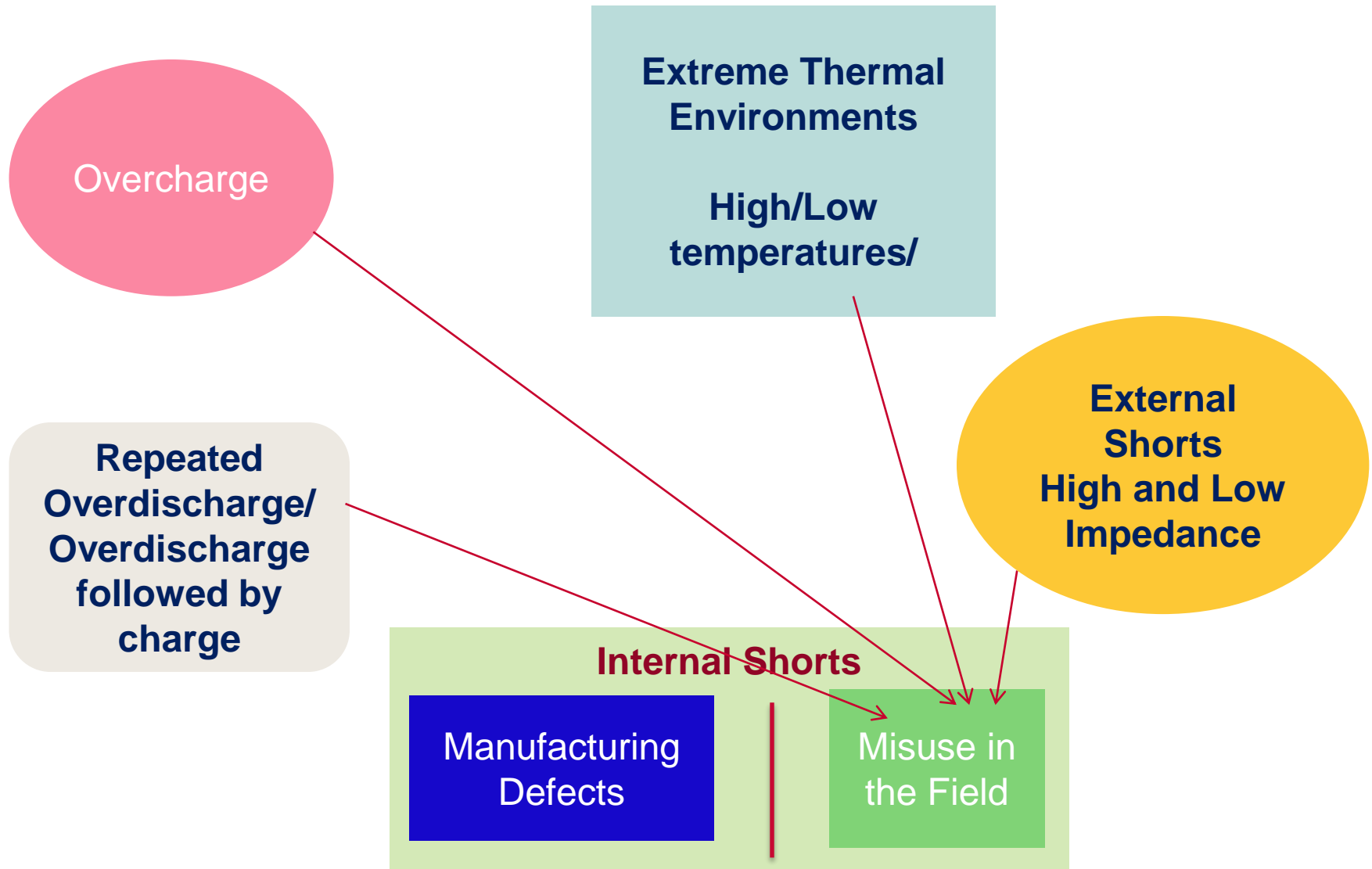
Transportation Safety

Toxicity

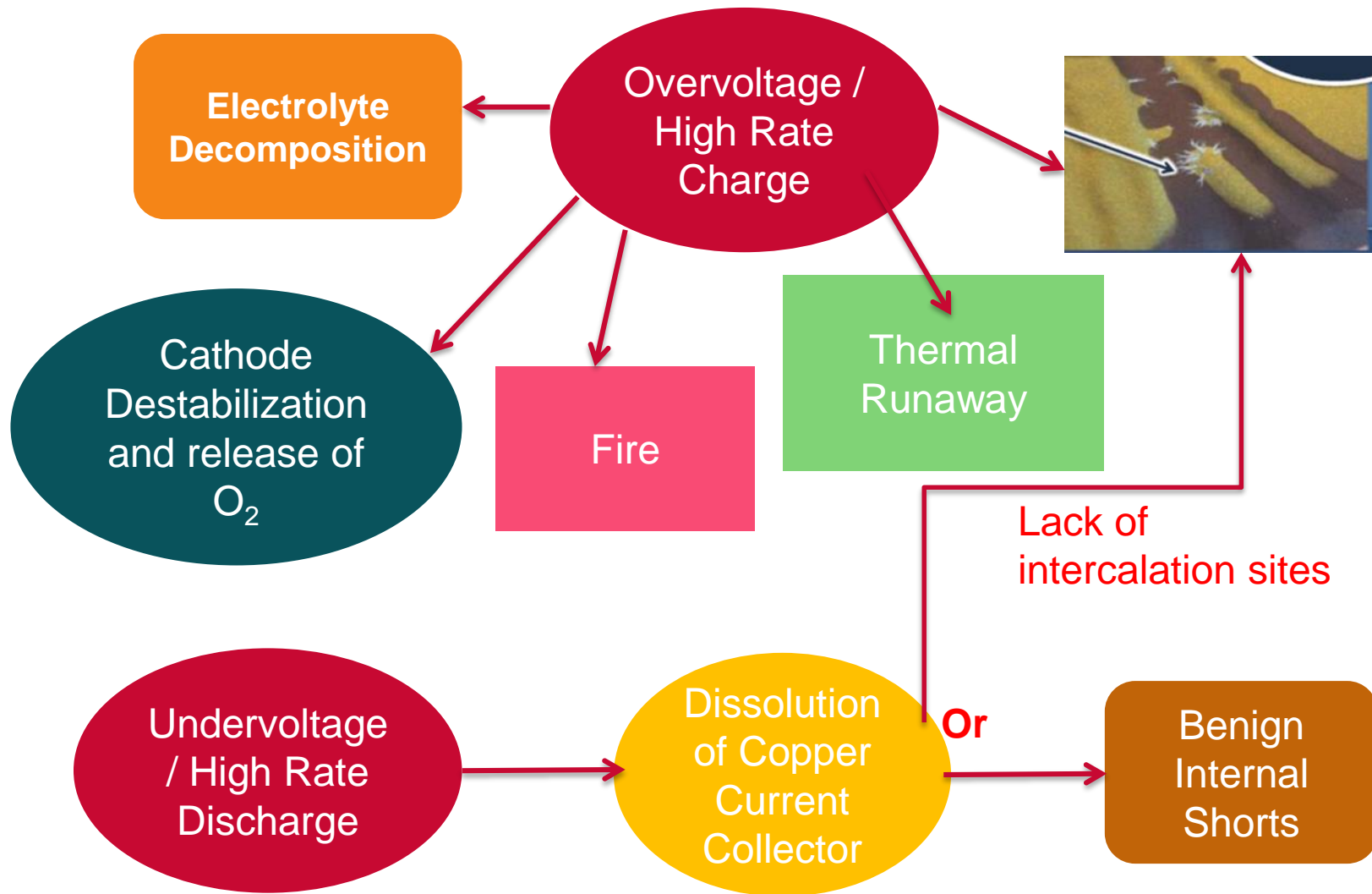
Environmental
Pollution



Lithium-ion Batteries: Hazards



Overcharge and Overdischarge Hazard Causes

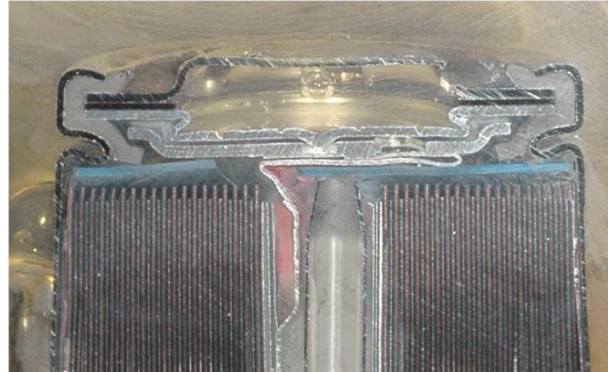


Cell Protective Devices and Limitations

Lithium-ion cells, whether cylindrical, prismatic, etc. irrespective of size, have different forms of internal protective devices

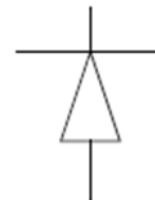
- PTC
- CID
- Tab/lead meltdown
 - (fusible link type)
- Bimetallic disconnects
- etc.

18650 Cell Cross-Section

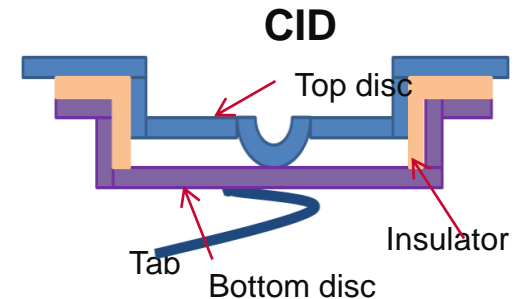


External protective devices used in lithium-ion battery designs are

- Diodes
- PTC/polyswitch/contactors
- Thermal fuses (hard blow or resettable)
- Circuit boards with specialized wire traces
- etc.

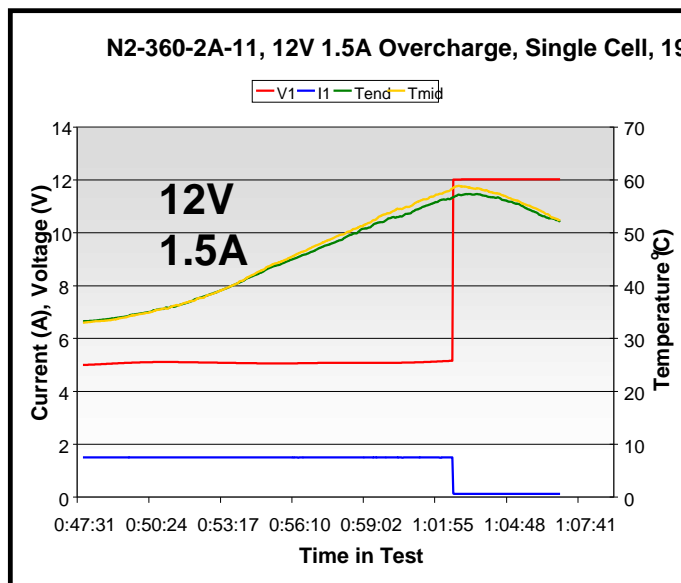


Diode

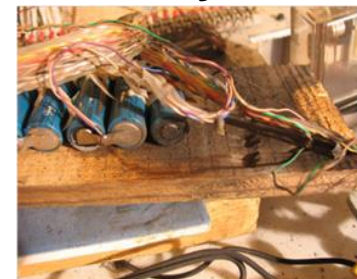
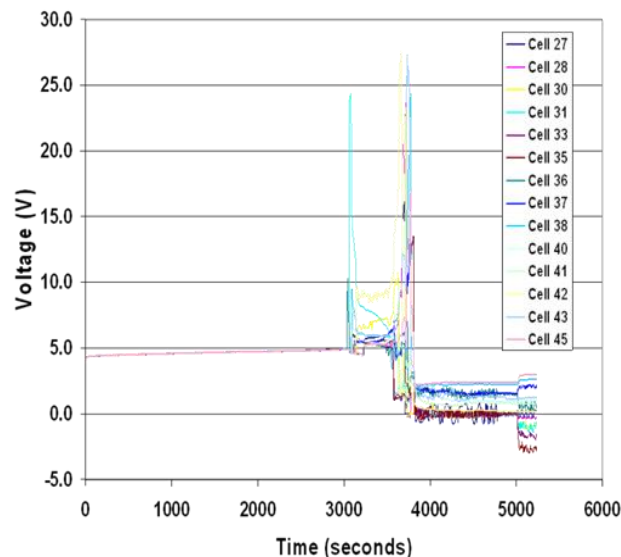


Overcharge Test on Single 18650 Cells and High Voltage (14S) String

Single Cell Test- no thermal runaway

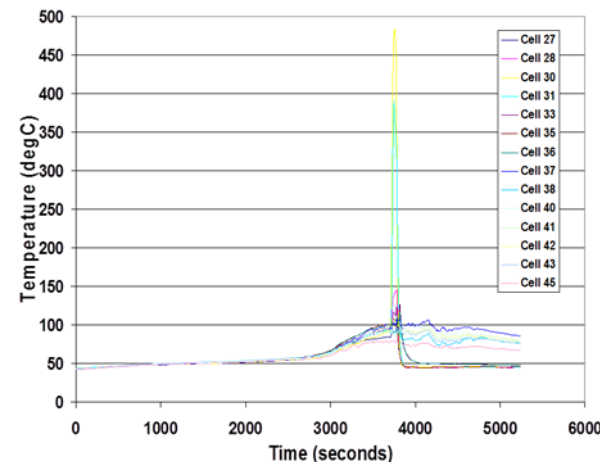


14S String Test – Thermal Runaway



Missing : 27, 28, 30 and 31

Cells 37, 38 and 45 showed no visible
Signs of venting



	CID Open Time (approximate)	Sample Temp. at CID Open (°C)
N2-360-2A-11	1:02:38	59
N2-360-2A-12	1:02:28	73

CID Activation - occurs reliably



External Short Circuit Hazard

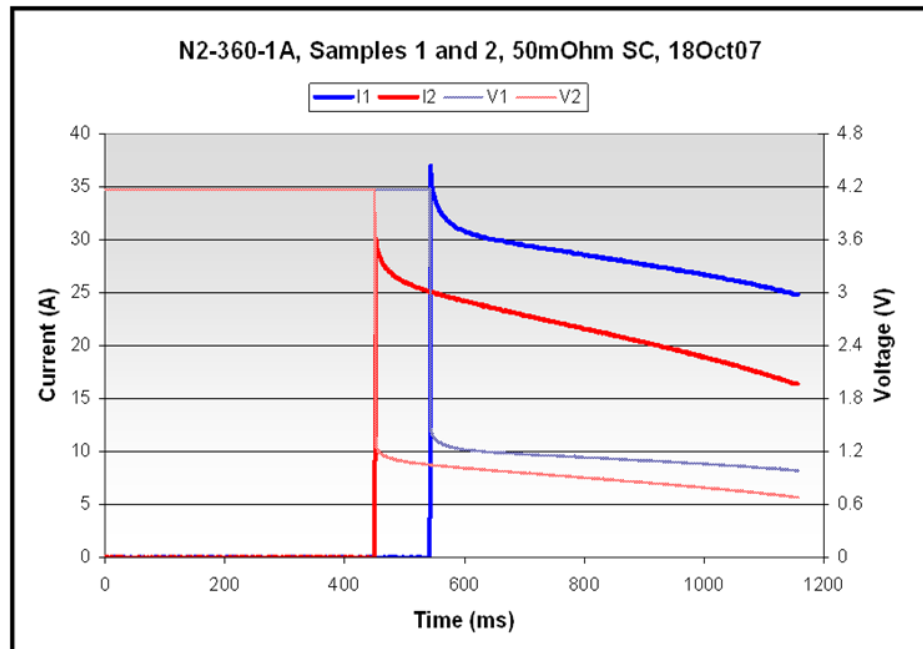
Electrical shock to the cell or battery from external sources.

Usually short circuit of very low resistance is observed.

Very high temperatures are observed.

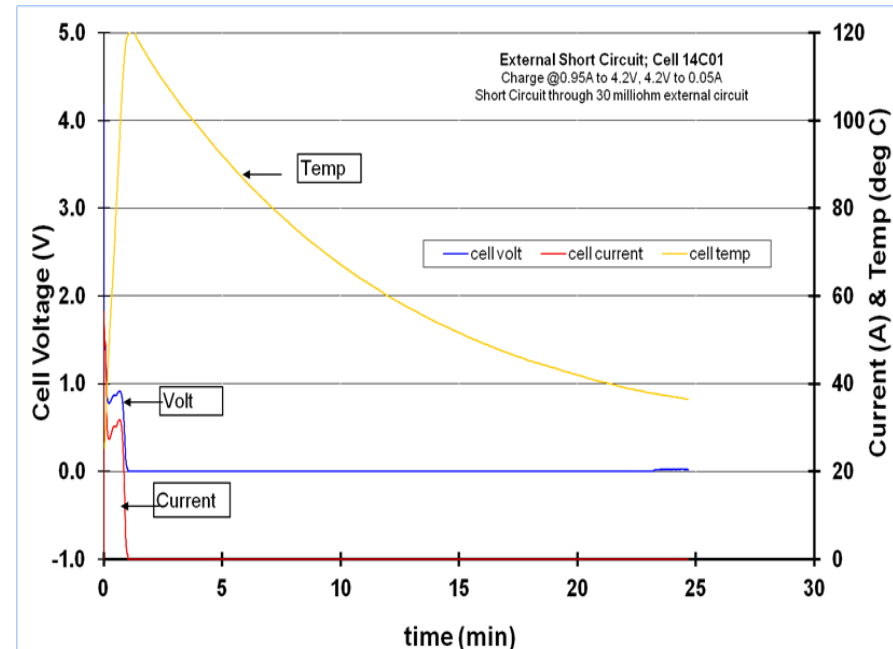
Venting and fire are also observed.

18650 Hard Carbon Cell – with PTC



PTC Activation - occurs reliably

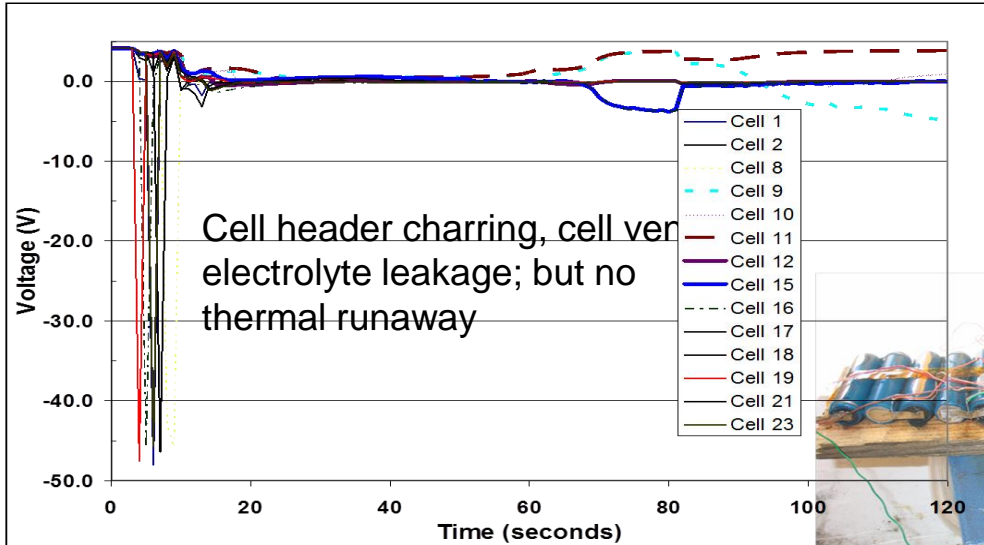
18650 Spinel Cell – without PTC



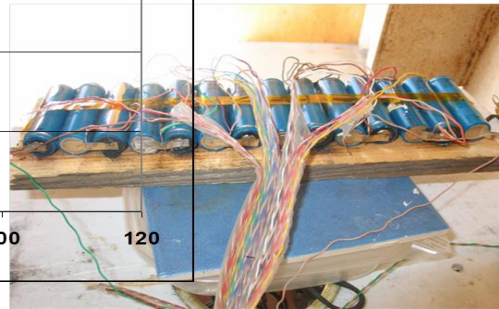
No venting, fire or thermal runaway

Multi-Cell Module Short Circuit Test on Li-ion Cells

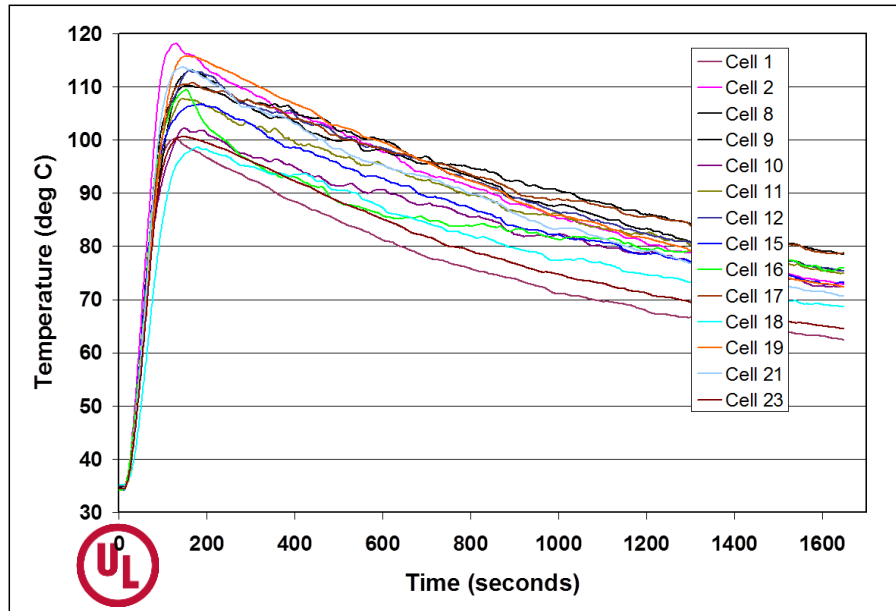
18650 Hard carbon cells with PTC (14S config.)



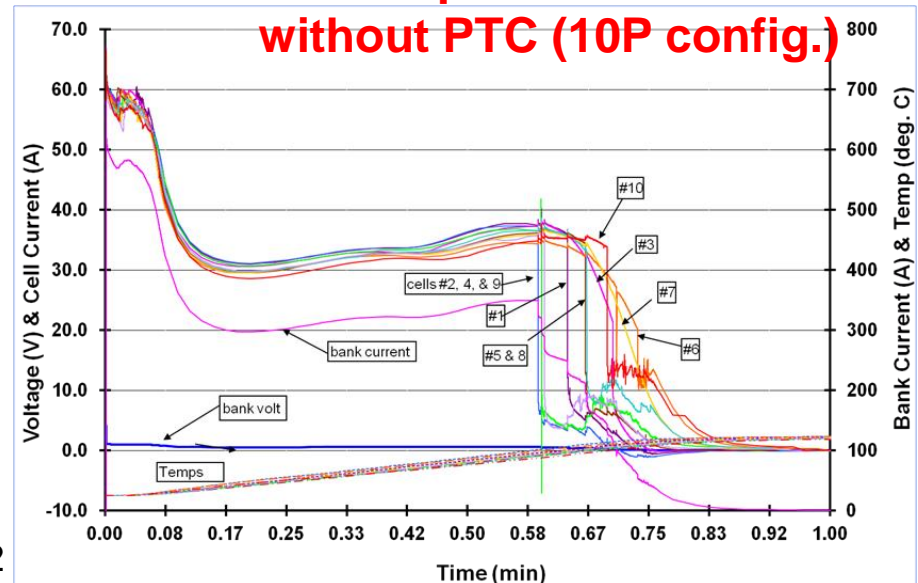
Only venting observed,
no fire
Cell Voltages in bold –
No visible signs of
Venting or damage,
but no voltage;
All others vented with
Obvious leakage or
discoloration



Rapid cell venting within the first 10 seconds



18650 Spinel Cells - without PTC (10P config.)



Internal Short Circuit Hazard

Short circuit that occurs inside a cell is called internal short circuit
Usually occurs due to defects inside the cell causing breakage of separator and consequently short circuit

Or it can be caused if the cell is used outside the manufacturer's specification.

High temperatures, venting and fire are observed.

Internal Short

- **Manufacturing Defect**
- **Field Failures**

Manufacturing Defect

Major defects screened by manufacturers

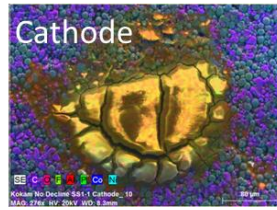
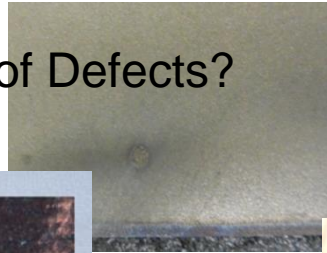
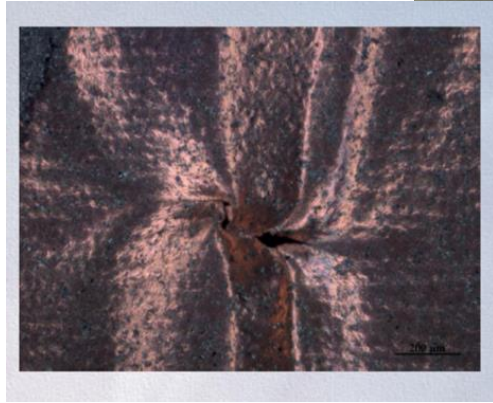
Subtle defects need to be identified and screened out during acceptance testing (for space applications these are called flight acceptance tests).

Field Failures

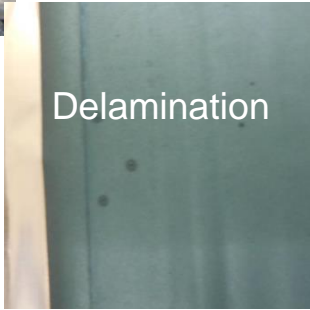
Avoided by **use within manufacturer's specification (I, V, T); stringent cell and battery selection and screening criteria; stringent monitoring and control (I, V, T); cell balancing, health checks (with issue- recognizable tests); good thermal design**

Nature of Defects Commonly Observed with Li-ion Cells

Chemical Analysis of Defects?



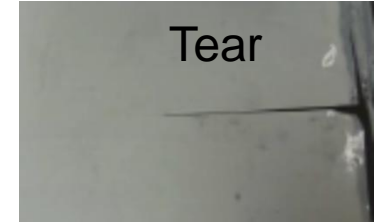
Delamination



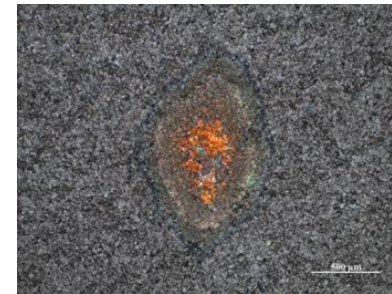
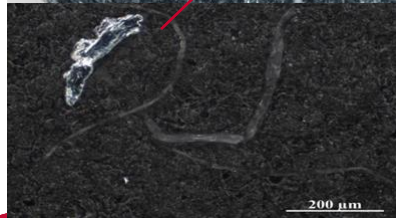
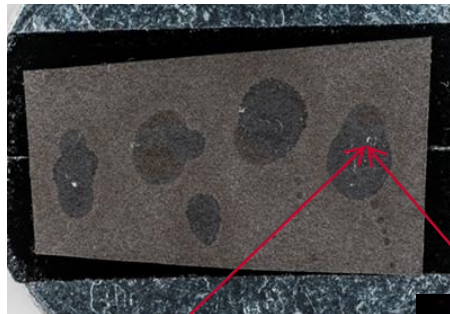
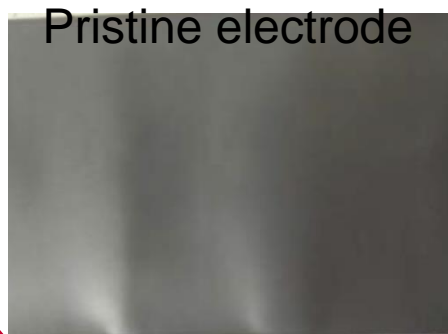
Salt Deposits ?



Tear



Pristine electrode



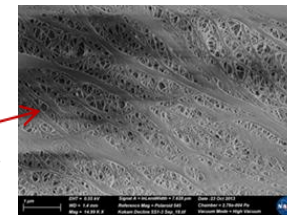
Iron particle



Zero porosity



Separator away
From defect
Showing porosity



High and Low Temperature Hazards

High Temperatures:

Electrolyte decomposition and gas production

Cathode and anode destabilization

Can lead to venting and fire.

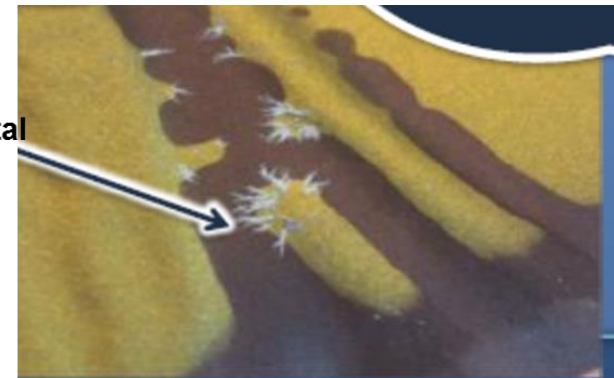
Low Temperatures:

Electrolyte viscosity increases

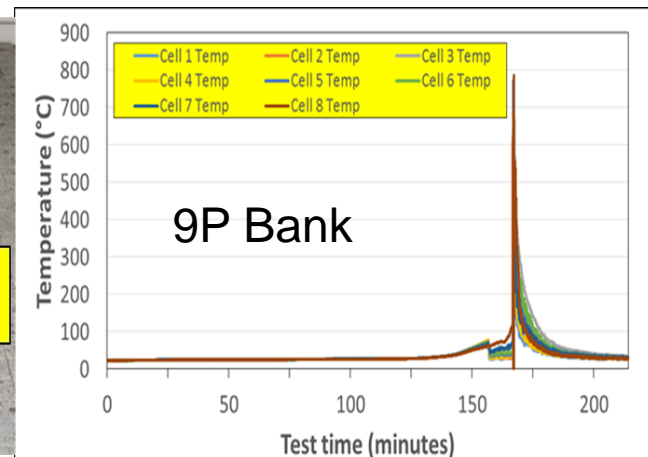
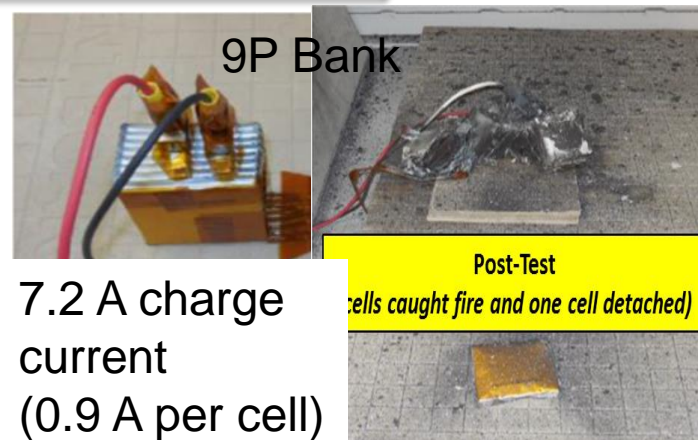
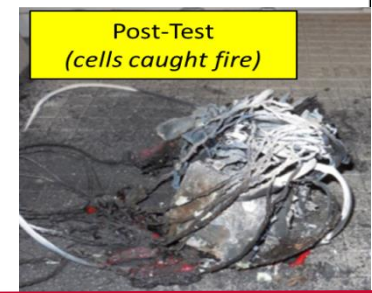
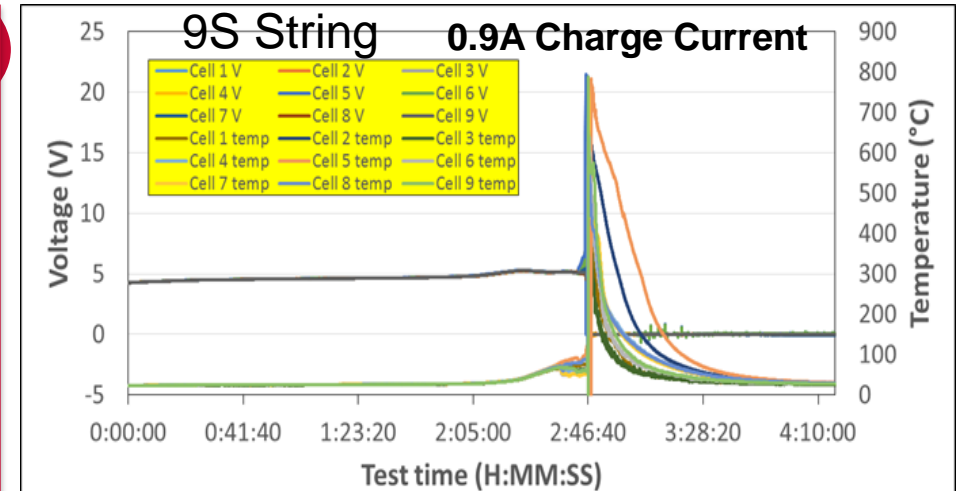
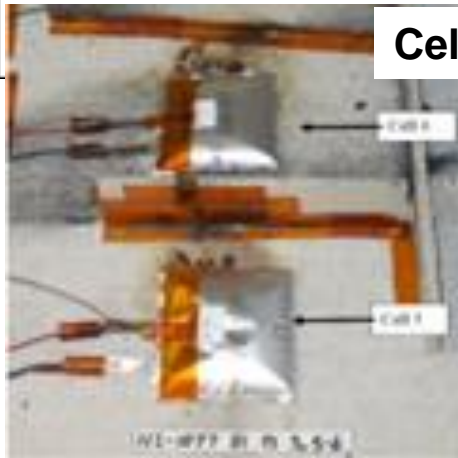
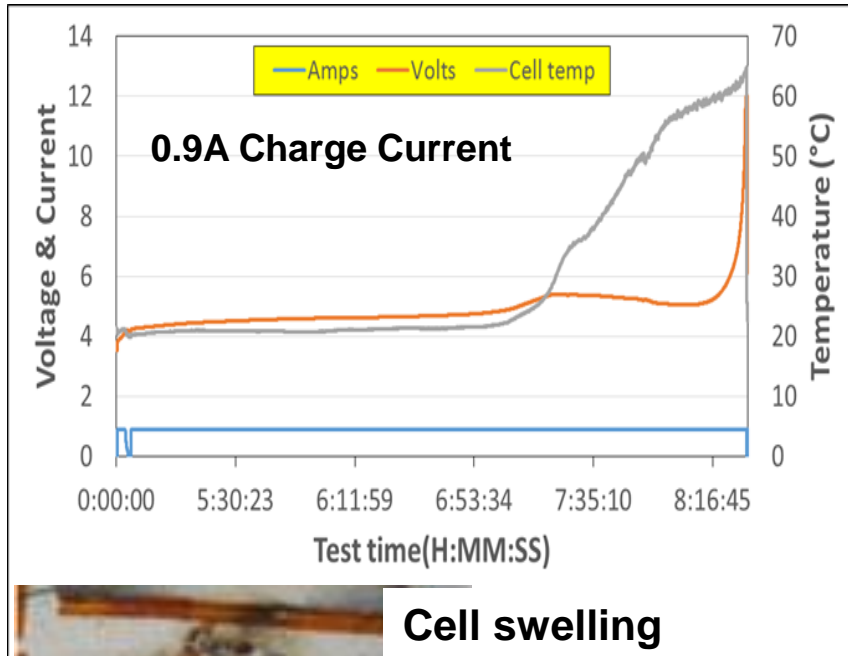
Increases resistance for the flow of ions

Can result in lithium metal dendrite formation

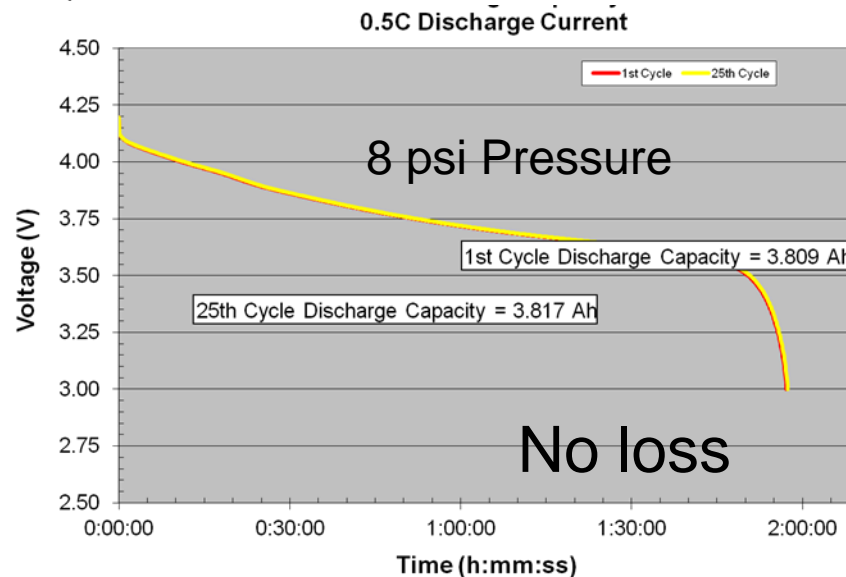
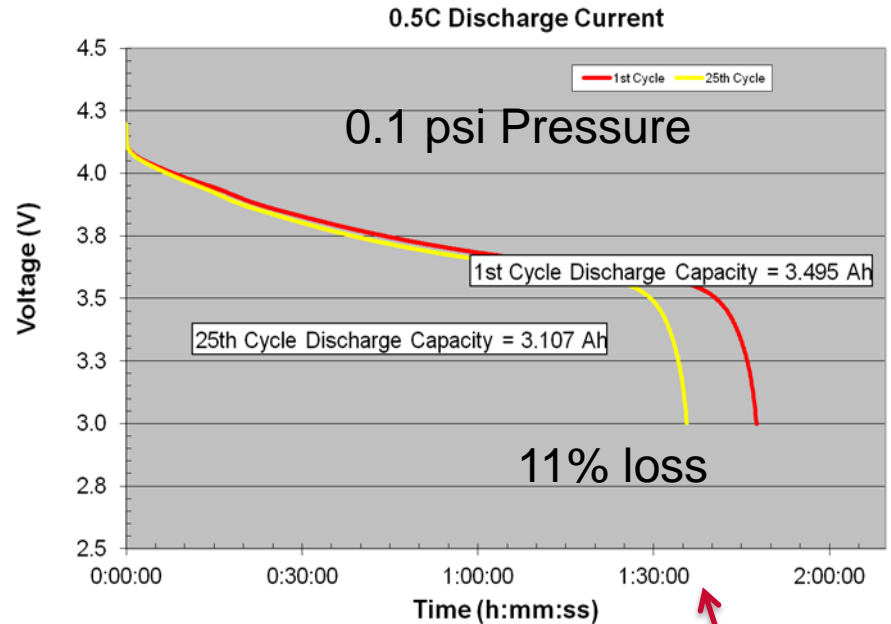
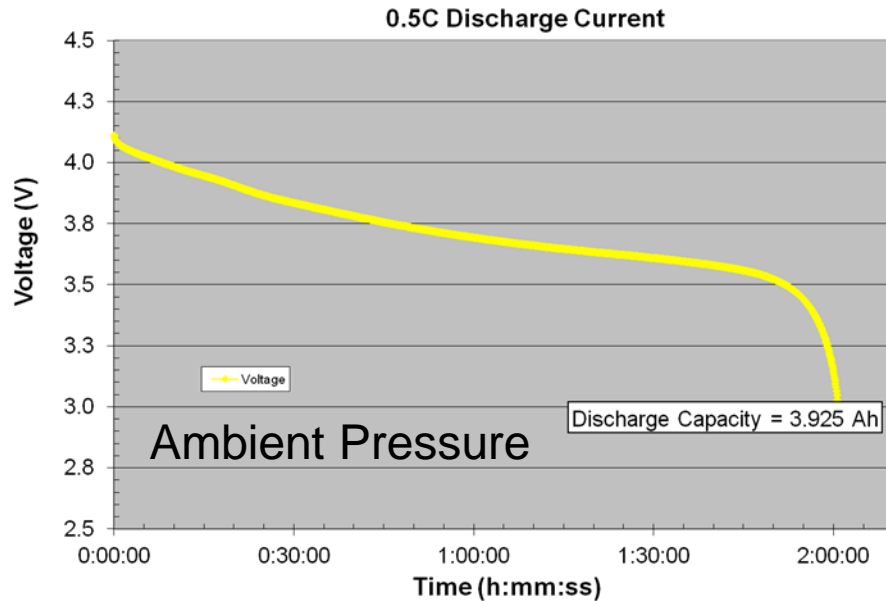
Lithium metal
dendrites



Pouch Cell Studies –Overcharge – single cell versus module (9S & 8P)



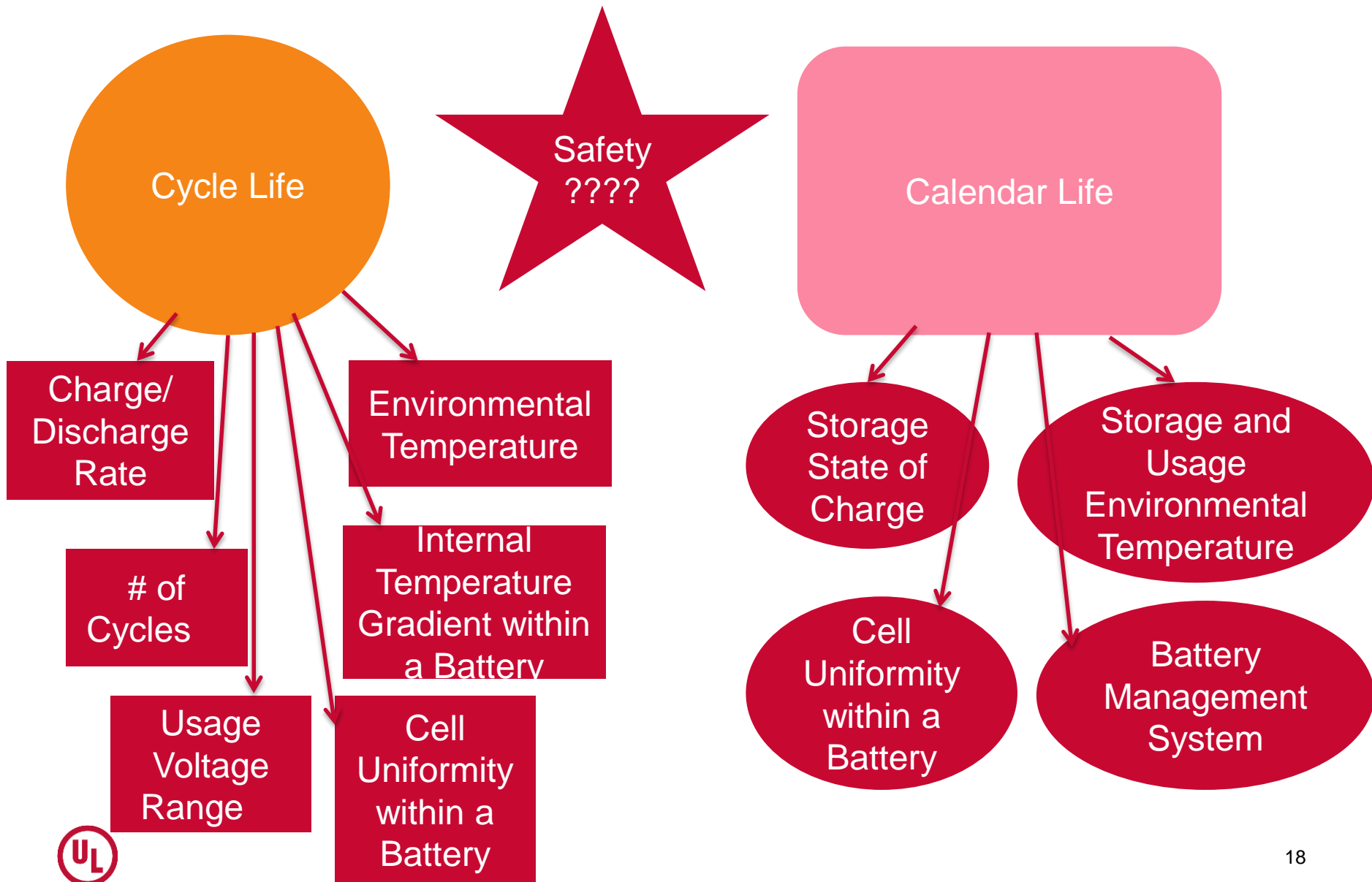
Pouch Cell Studies –Ambient; Vacuum and Low Pressure Environments



25 cycles



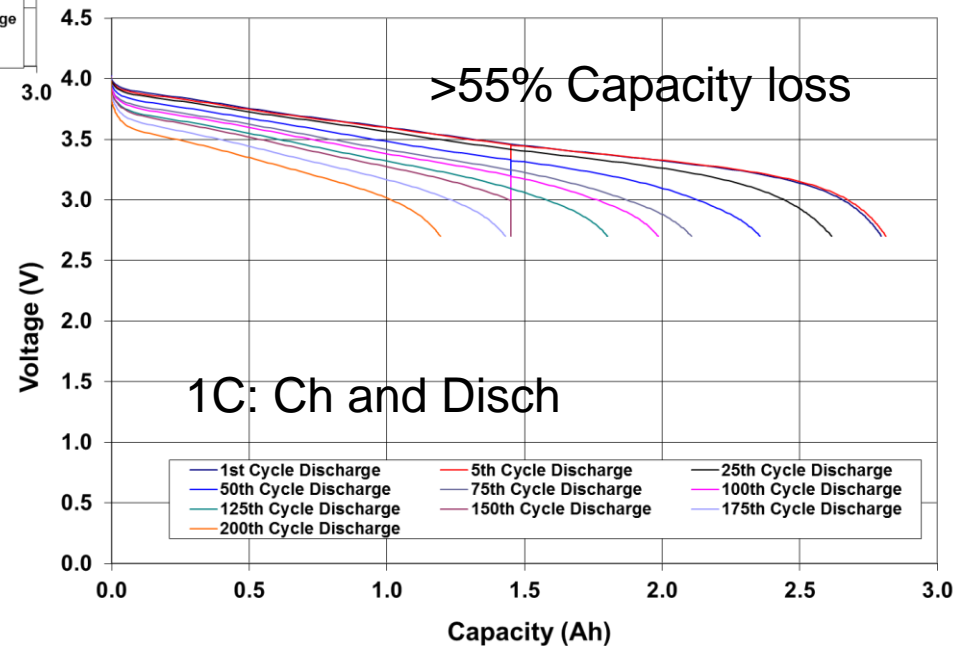
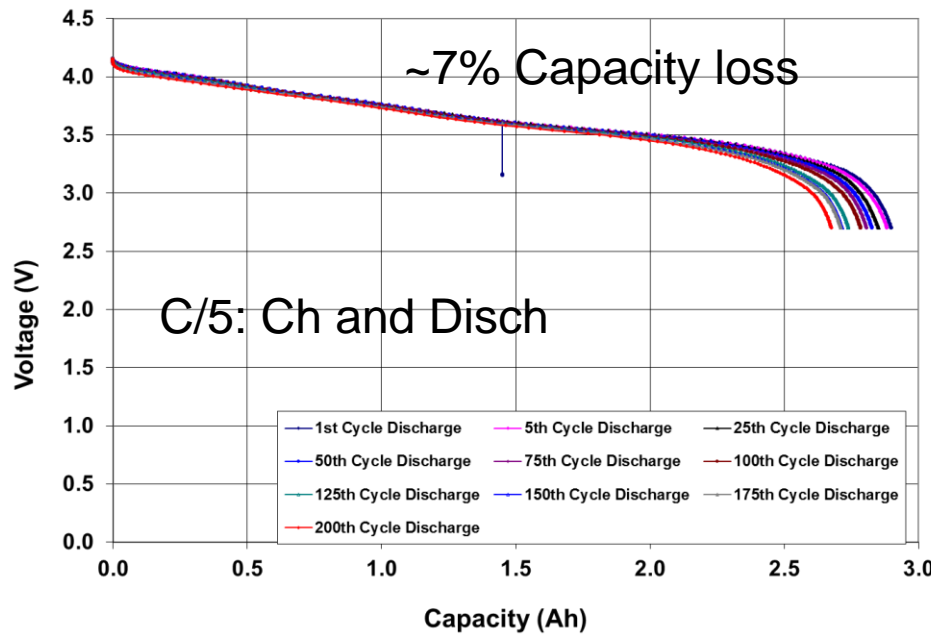
Factors Affecting Aging and State of Health



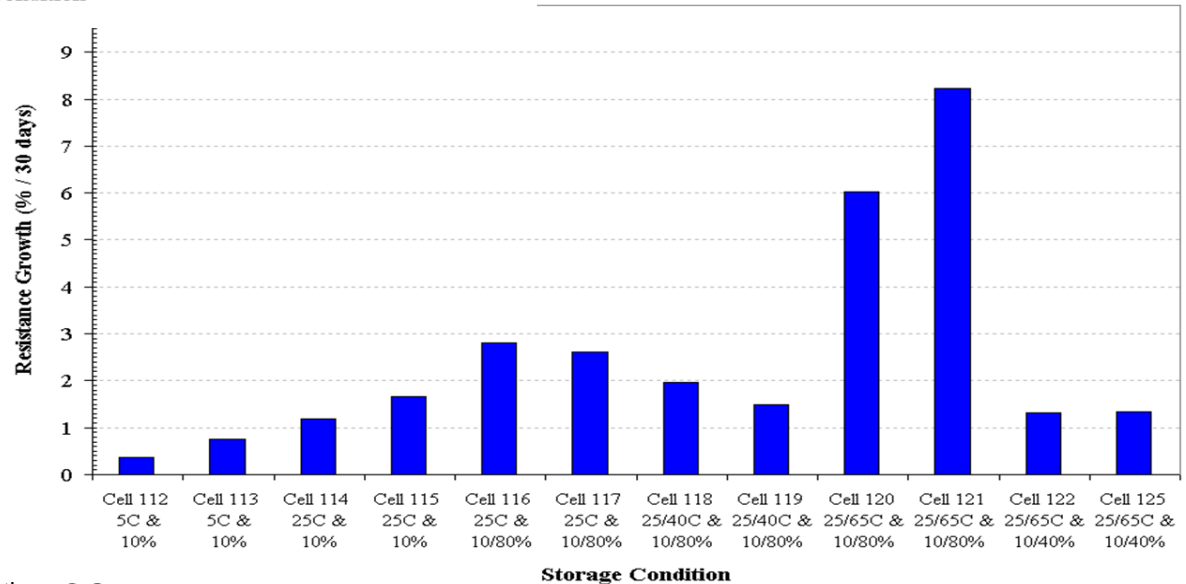
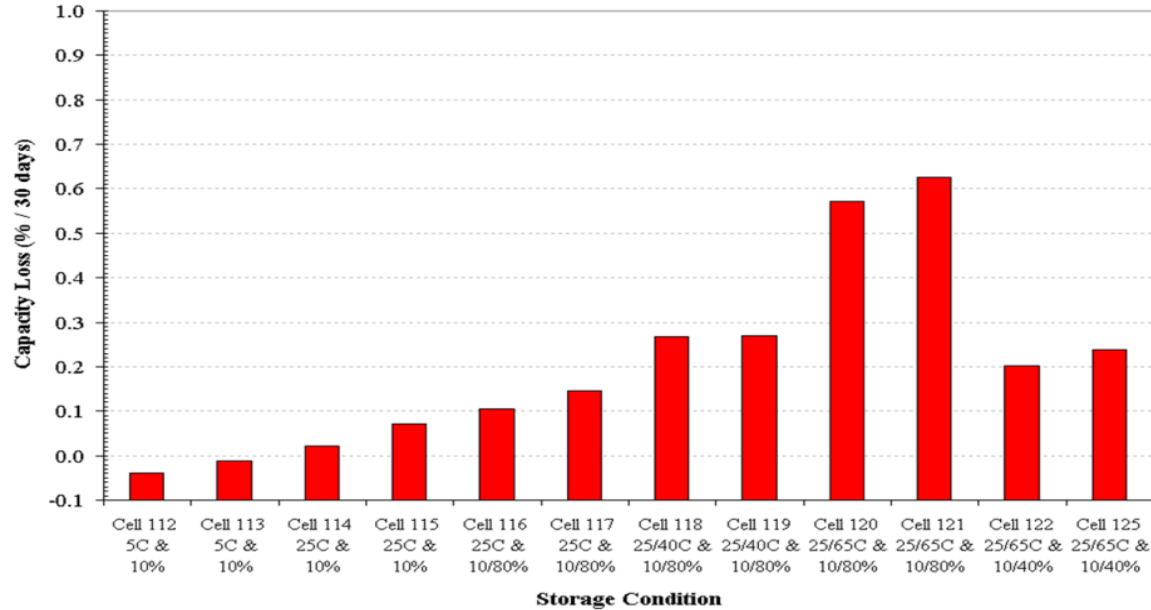
Aging Effects on Cell

- **Lithiation and de-lithiation causes**
 - Anode electrode morphology changes and volume changes – surface can form cracks leading to electrical isolation; delamination from current collector; changes in intercalation kinetics; loss of active lithium inside anode, etc.
- **Decomposition**
 - Binder and electrolyte; SEI decomposition; HF production, li-ion side reaction with electrolyte; etc.
- **Corrosion**
 - Current collector, cell can materials, pouch cell swelling and shorting due to corrosion of pouch material, etc.
- **Cathode changes**
 - Structural disorder, metal dissolution, disproportionation, etc.

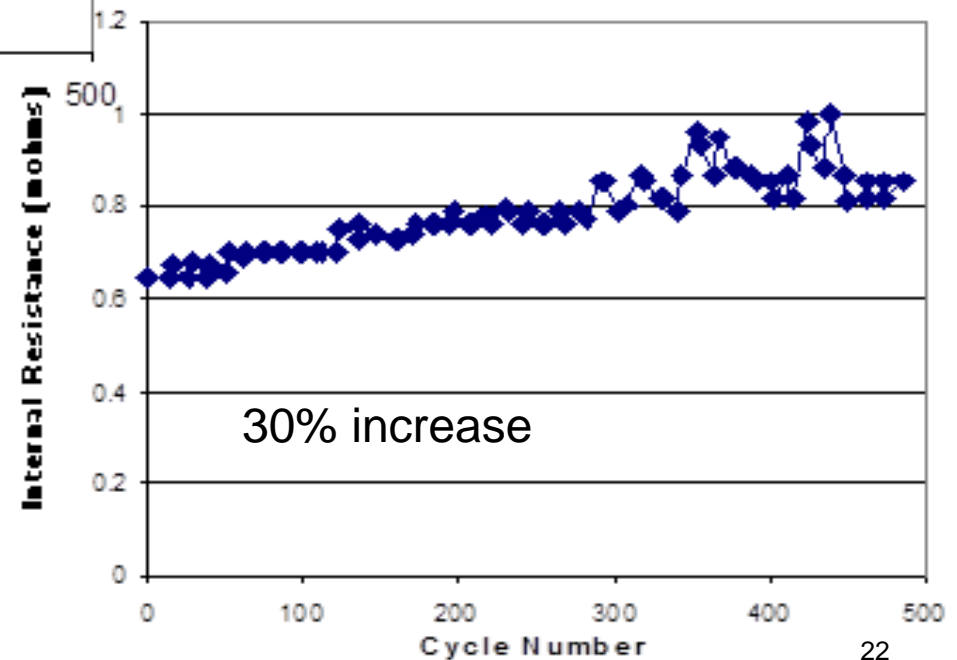
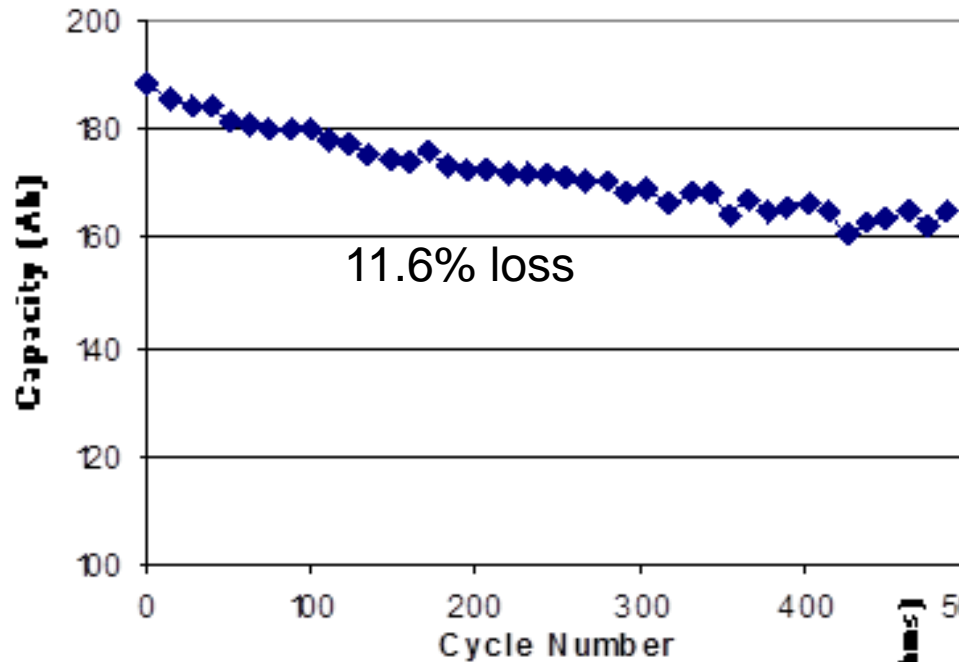
Cycle Life Performance at Different Rates



Capacity Loss and Internal Resistance Growth for Cells Used in Orbiter Upgrade Study

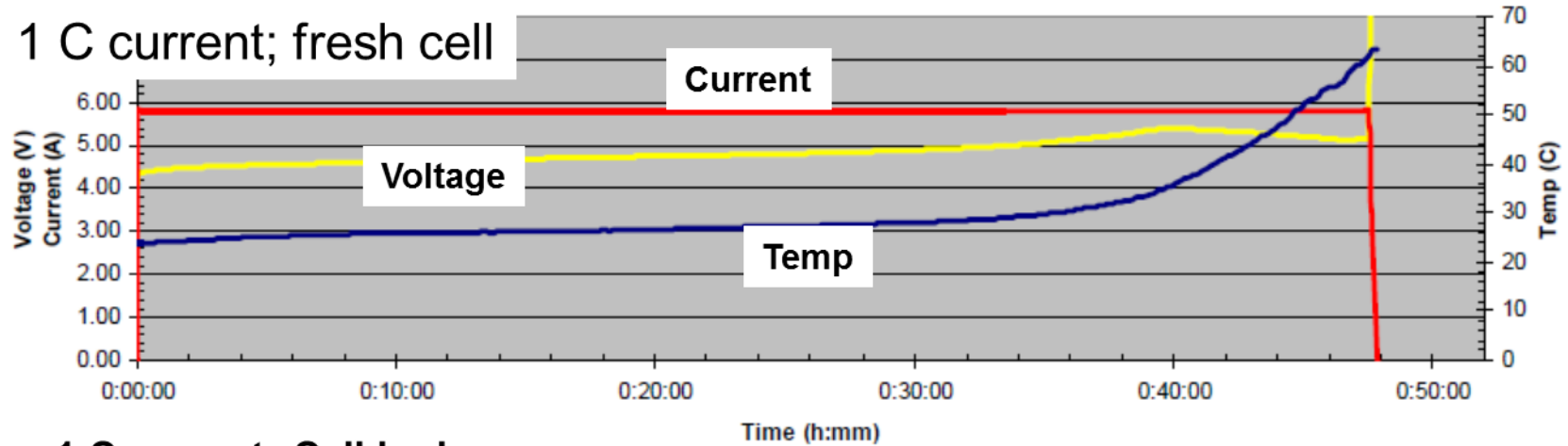


Cycle Life Studies on Li-ion Cells Under Orbiter APU Upgrade Study

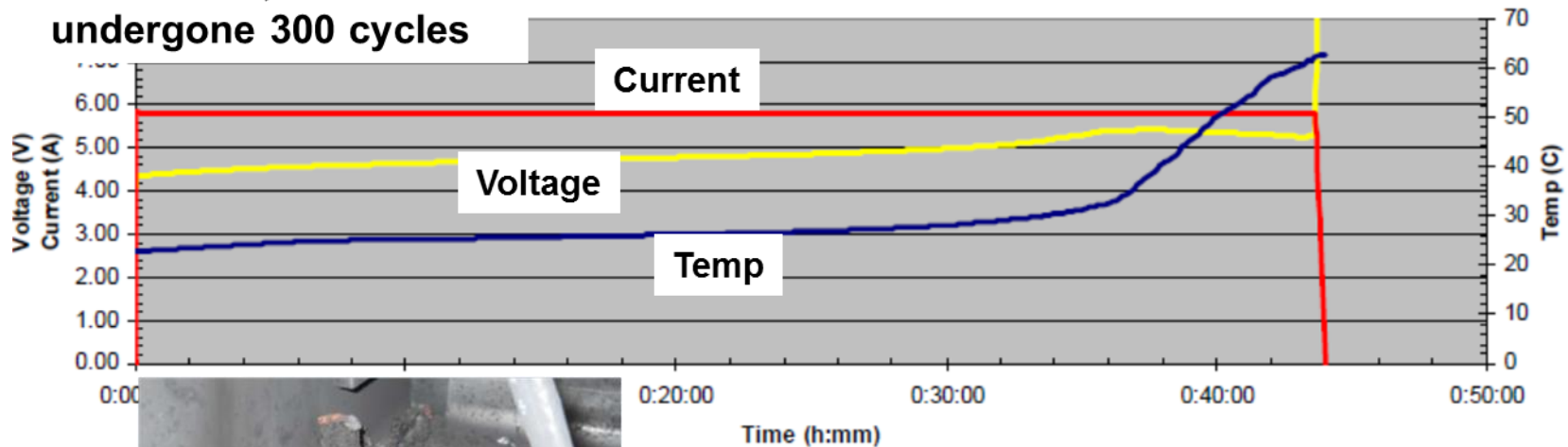


Safety after Cycling - Overcharge

1 C current; fresh cell



1 C current; Cell had undergone 300 cycles



3.1 % Capacity loss after 300 Cycles

J. Jeevarajan, 222nd ECS Meeting, October 2012



Cycle Life Aging and Simulated Internal Short Tolerance

- **Cells were cycled at 1C rate of charge and discharge for 1000 cycles**
 - **Cells lost capacity between 12 to 25%**
- **Conducted Simulated Internal Short (SIS) tests (Crush test method) - Sample size – 10 cells**
 - **Tolerance to simulated internal shorts increased with higher loss in capacity– no fire or thermal runaway observed even with cells that lost greater than 19% capacity (SIS performed at 100% SOC); cells that lost between 12 to 16% capacity went into thermal runaway (SIS performed at 100 % SOC)**

Note: All fresh cells at 100 % SOC when subjected to simulated internal short went into thermal runaway



Current Studies: Test Plan – UL/Texas A&M University

- **Single Cell Studies**
 - Cycle life with continuous cycling at normal voltage range
 - Cycle life with continuous cycling with reduced voltage range (200 mV less from both ends of voltage range)
 - HEV profile at 3 temperatures
 - **Overcharge and external short test on fresh and cycled single cells**
- **Module (3P9S: 9.9 Ah, 33.3 V) Studies**
 - Cycle life with continuous cycling at normal voltage range
 - Cycle life with continuous cycling with reduced voltage range (200 mV less from both ends of voltage range)
 - HEV profile at 3 temperatures (10 °C, 23 °C and 45 °C)
 - **Overcharge and External short test of fresh and cycled modules**

Destructive Analysis:

Fresh cells : uncycled, externally shorted cell and overcharged cell

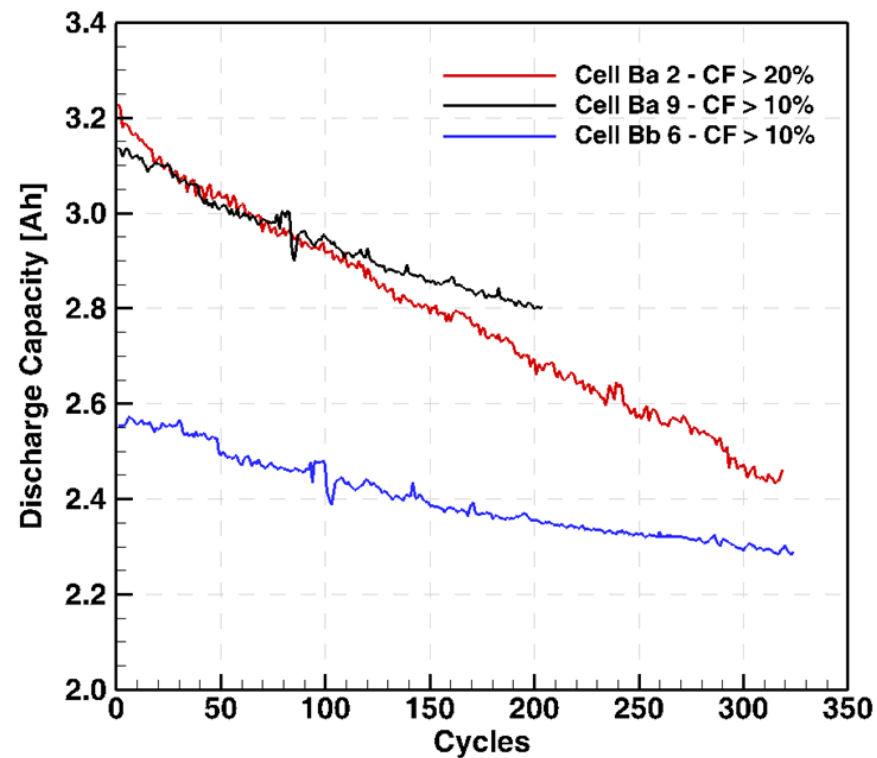
Cycled cells: cycled (cells removed after set number of cycles), externally shorted cycled cells, overcharged cycled cells

Fresh modules : uncycled, cells from shorted and overcharged modules

Cycled modules: cycled, cells from shorted and overcharged modules



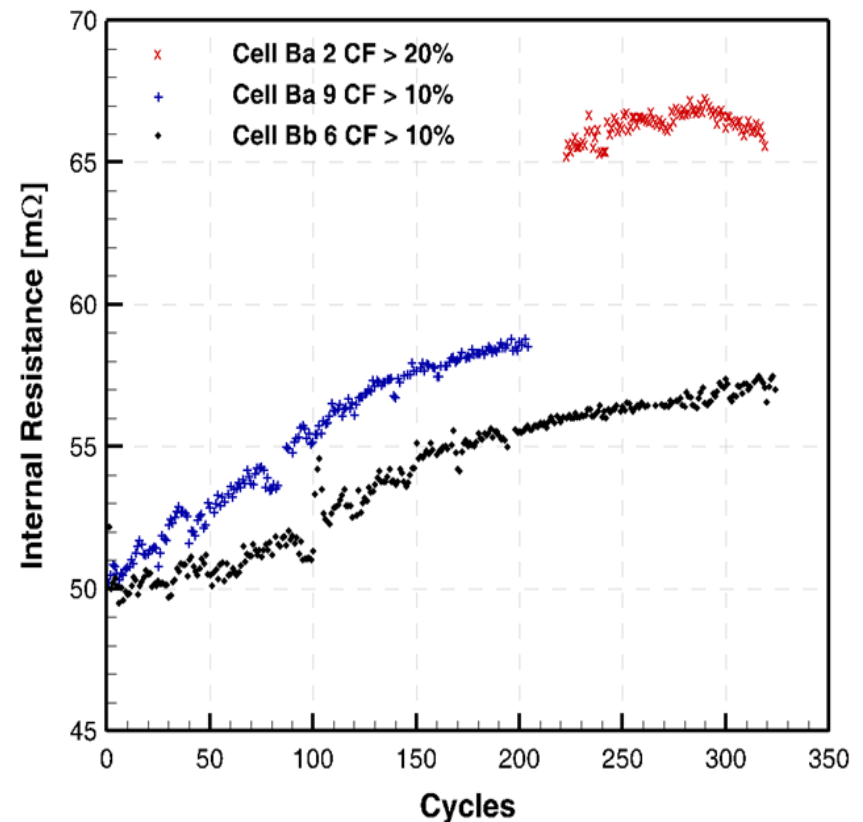
Capacity and Internal Resistance Trend with Cycle Life



Test Protocols:

Ba: CC/CV with EOCV of 4.2 V
Discharge to 2.7 V

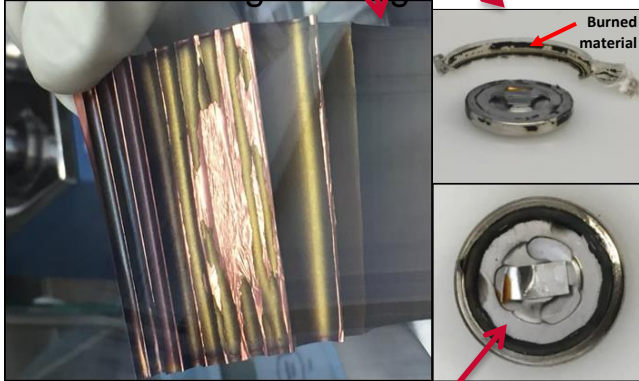
Bb: CC/CV with EOCV of 4.0 V
Discharge to 2.9 V



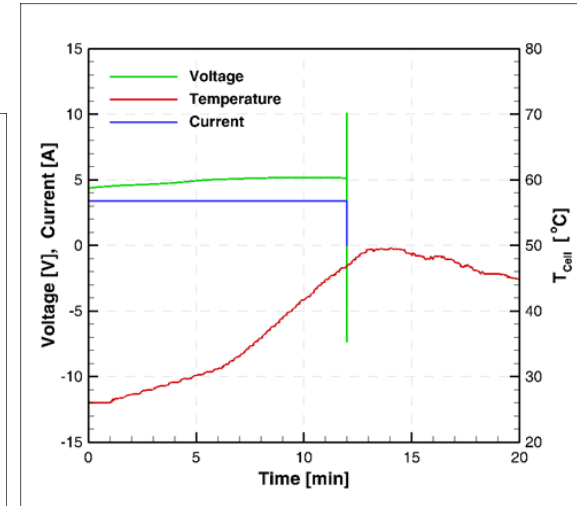
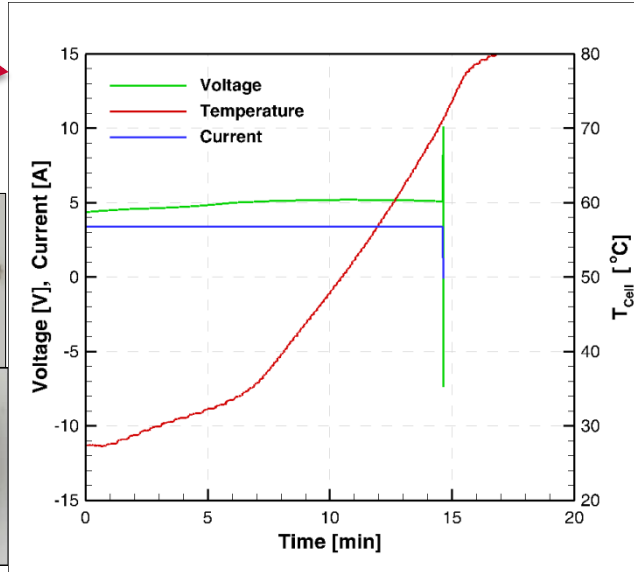
Challenges with Cell Safety Features

Overcharged cell (fresh cell) with delayed CID activation

Anode showing charring

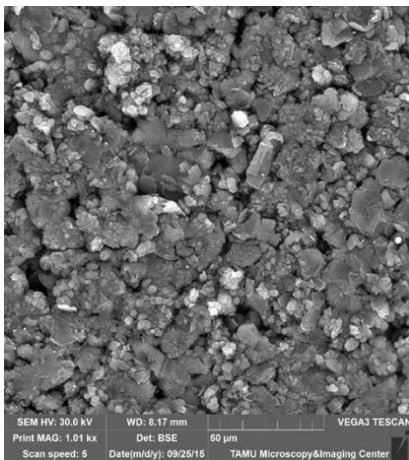


Cell header (underside) showing charring



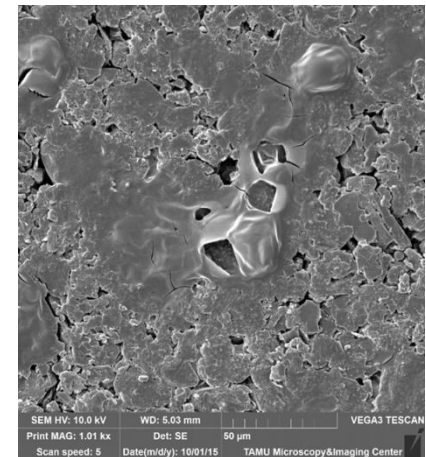
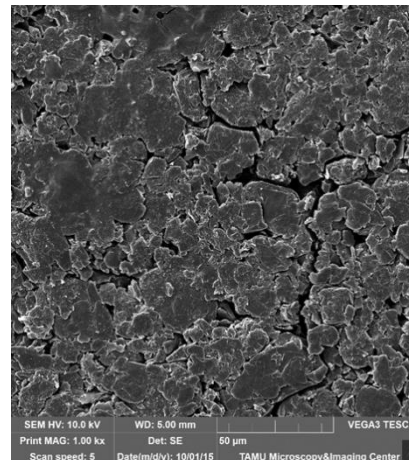
Cell with normal CID activation

Anode of Fresh cell



Cell exhibited PTC activation

Anode surface of fresh (not cycled) externally shorted cell



Approaches for Safe Designs for Use and Transportation

- Use **within manufacturer's spec for voltage, current and temperature**

OR

- **Qualify with ample margin to requirements;**

• Reducing voltage range used by application increases battery life, health and safety

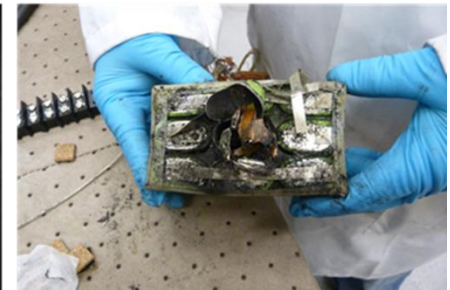
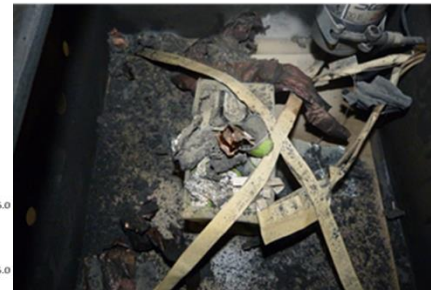
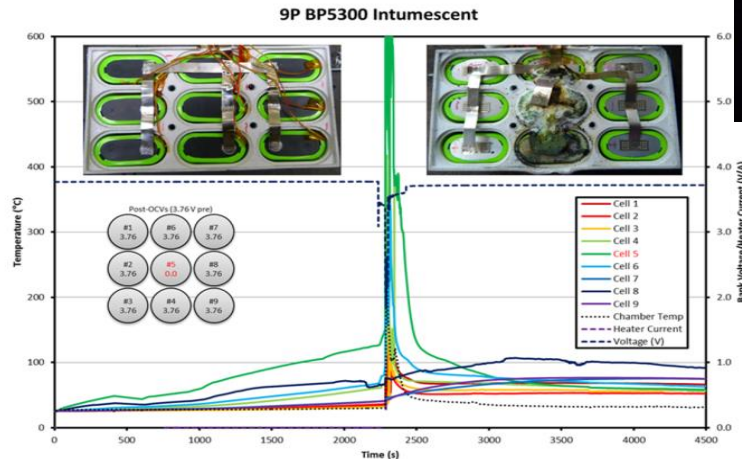
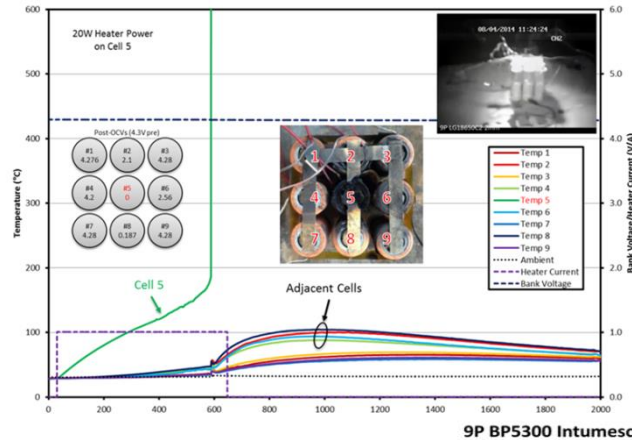
- **Complete characterization of performance and safety** of lithium-ion cells and batteries should be carried out to carve out the baseline (qualification of design)
- **Test stringently** and extensively in the **relevant configuration** and **environment** to understand and **characterize the safety controls and their limitations.**
- Carry out high fidelity thermal analysis and design with best heat dissipation paths



Approaches for Safe Designs for Use and Transportation

Prevent Cell to cell thermal runaway propagation

- Cell to cell spacing; barriers between cells, etc. to prevent cell to cell thermal runaway in the unlikely event of single cell thermal runaway.
- Use of extinguishers and other fire suppression methods installed internal to battery container.



Methods to Determine Module Health Before Second Life

Test and Destructively Analyze sub-module:

- Using **high fidelity thermal analysis** for the battery/module design, the module exposed to worst case thermal deviations should be chosen for testing (as it will not be reused)
- Carry out voltage, capacity and internal resistance/ac impedance tests
- Carry out cell to cell interconnects' integrity tests, complete visual inspection and voltage measurements on each cell /cell bank
- Disassembly of module followed by measurement of cell voltage, capacity of individual cells, internal resistance and ac impedance tests
- Disassembly of cells to study electrodes and electrolyte; three electrode cell studies
- Safety tests at the module and cell level to study any variations in safety characteristics between used and baseline values (inclusion of ARC along with electrical safety tests will add value)

Methods to Determine Module Health Before and During Second Life

For Modules to be reused:

- Visual inspection (should include internal component inspection), voltage, capacity, internal resistance/ac impedance
- Functional checks for proposed new second-use application and environment – run profiles in the relevant environment to confirm that module can perform as required
- Functional checks through complete process of assembly and after assembly into stationary energy storage configuration for utilities.
- Continuous monitoring of health of the cells, modules, battery and system to look for anomalies – allows for early problem detection
- Confirm that charger is suitable for the age of the battery

Summary

- Complete characterization of performance and safety of lithium-ion cells and batteries should be carried out to carve out the baseline (qualification of design)
 - Test stringently and extensively in the **relevant configuration** and environment to understand and characterize the limitations.
- Use **Stringent screening methods** for cells and batteries.
- Being **vigilant of off-nominal behavior and recognizing** this during the life of the battery is a critical part of removing defective cells/batteries from service before they go into a catastrophic failure mode. More important for long term usage batteries.
- Lastly, **usage limits, appropriate monitoring and control, cell balancing and thermal design** are key to prevent subtle defects from turning into nucleation sites for larger fault conditions.
- **Analysis and modeling** are ways to lower cost of testing large modules and batteries; however, full scale safety testing should be carried out with the final full scale battery design
- **Test, design, retest, redesign,.....dynamic pattern is required for confirmation of safety**



Acknowledgment

Texas A&M University team for current collaborations with UL:

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Daniel Robles

Chien-Fan Chen



THANK YOU.

